PETROLEUM COKE HANDLING PROBLEMS

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INTRODUCTION

Calcined petroleum coke is an industrial carbon which is used as a raw material in the Aluminum Industry and the Graphite Industry. From the time it is first formed as a by-product of petroleum refining until it is finally processed into elemental carbon it is handled many times. Extreme care must be exercised at each point of handling in order to preserve the desired physical structure and maintain the required degree of purity. This paper reviews the steps used in the carbon industry to achieve these objectives.

Quality Considerations

Calcined petroleum coke is a commodity which must be delivered to the ultimate consumer in a size range which will permit an adequate proportion of coarse particles. This is necessary in order to meet the formulation requirements in a carbon paste mix. It must also be free from contamination.

Formation of Petroleum Coke

Raw petroleum coke is a by-product from refining of petroleum residuals. One of the procedures by which this is accomplished is known as the delayed coking process. This gives a coke with a sponge-like structure. Other methods such as the fluid coking process are also used but the product from this operation does not have the structural properties required for use in the Aluminum Industry or Graphite Electrode Industry.

Figure 1 shows a cross section of a coke drum and illustrates how the coke is formed in the delayed coking operation. The drum is a large insulated vessel about 20 feet in diameter and 70 feet high. The coke is formed at the rate of about 2 feet per hour and proceedes to build up during a 24 hour cycle. The material at the bottom is fully polymerized and develops a porous structure through which gases and liquids can pass. The top layer in the coke drum is not fully polymerized until it is subjected to heat for a prolonged period of time.

At the very top, some foam occurs. This foam subsides during the steaming and cooling cycle. It is important in filling the coke drum to avoid any carry over of foam or pitchy material into the vapor lines. Foam depressants are used to minimize the amount of foam (1). Level indicators are used to establish the position of the liquid or foam in the drum (2). These are operated by transmitting a beam from a radioactive source to an instrument mounted near the top of the drum. When the liquid reaches a predetermined level the feed to the drum is switched to an empty drum. At this time the full drum is steamed to remove light hydrocarbons and finally cooled by introducing water at the bottom of the drum.

Factors affecting Sizing of Coke

The coke is removed from the drum by means of high pressure water jets which operate on the principle used in hydraulic mining of coal (3). The procedure used in cutting the coke from the drum is extremely important. If it is not carried out properly the physical structure of the coke will be destroyed and the ultimate consumer would not have enough coarse particles to balance out their carbon aggregate formulation. The recommended procedure for cutting the coke is illustrated in Figure 2. This series of diagrams shows the steps which should be taken in order to get the maximum amount of lump coke needed for further processing.

The first step is to bore a pilot hole. During this operation the fine cuttings are held in the upper section of the drum until the hole is completely through the bottom. At this time, all of the center cuttings fall out of the drum together with the water used in cutting.

The drill stem is raised to the top and the bit is changed to a cutting head which has nozzles directed in a horizontal manner. The pilot hole is enlarged so that lumps of dislodged coke can fall freely through the opening. This avoids the danger of a coke build up around the drill stem which would prevent the rotation of the cutting head.

Once the pilot hole is enlarged the stem is raised to the level of the coke in the drum. The operator can tell by the sound of the water hitting the metal walls when the top is reached. At this time the stem is lowered 3 - 4 feet below the top. It is held in this position for several minutes until the coke is undercut. Then the stem is raised and lowered rapidly within this section until the coke is all cut from this layer. This action causes the coke to collapse from the drum walls resulting in large pieces which fall through the pilot hole. This operation is repeated until the drum is completely empty. In general, the decoking operation requires about 3 to 4 hours depending on the hardness of the coke. The harder the coke the more time required.

Lump coke in the size range of baseballs to footballs can be handled easily in conventional conveying systems. At the calcining plant all coke is run through a roll crusher set at an opening of 4 inches before it is fed to the kiln. The tumbling action in the kiln results in further degradation so that the final product all passes a 1 inch screen with approximately 35 to 40% retained on a ¼ inch screen.

Procedures to avoid Contamination

There are several systems used in handling coke after it is discharged from the drum. These are as follows:

A. The coker is mounted over a railroad track so that coke can be discharged directly into open hopper cars or gondola cars.

B. A roll crusher is placed below the drum on small tracks. This breaks up the large lumps to a size which will permit a coke slurry to be transported by pumping through a pipe line.

C. The coke is directed to a ramp which leads to a pit. The pit may or may not contain water for further cooling of the coke.

In each of the above systems it is necessary to provide for the recovery of water used in cutting. The areas around the coking unit should be paved. Curbs and retaining walls should be provided to contain any coke spillage. The drainage around the coker must be carefully planned to avoid sand, clay and gravel from entering the system. Drainage from rainstorms should be directed away from the coking unit.

Transporting and Conveying Coke

The freight cars used to transport the coke should be clean. Any sand, gravel or iron rust will contaminate the coke. The cars should be carefully inspected before loading.

When coke is unloaded at the calcining plant, it is either conveyed directly to a storage silo or to an outdoor storage. When outdoor storage is necessary, it is preferable to provide paved areas to minimize contamination. The activities in the surrounding area can also affect the purity of the coke. For example, unloading of iron ore in the vicinity will contaminate the coke pile under certain wind conditions.

Magnetic separators are used at the calcining plants. These will remove scrap iron from green coke, but will not remove iron rust, since the latter is non-magnetic. During calcining any iron oxide (rust) will be reduced to iron which can be removed from the calcined petroleum coke with magnets.

Chemical Composition of Petroleum Coke

Green petroleum coke from the delayed coking process is essentially a hydrocarbon. The chemical composition as obtained by an ultimate analysis is given in Table I. Before it can be used as a carbon aggregate it is necessary to convert the green coke into elemental carbon by a petrochemical process. This is carried out by a pyrolytic treatment at temperatures around 2300°F. In this operation the carbon is not developed until hydrogen is chemically removed by thermal decomposition. In the trade this process is referred to as calcination, but it is essentially a dehydrogenation reaction which converts a hydrocarbon into elemental carbon as indicated in Table I.

A number of changes in basic properties and structure are brought about by the removal of chemically bound hydrogen from the hydrocarbons in order to produce elemental carbon. Some of these are as follows:

A. The real density of green petroleum coke is 1.30. After calcining the real density is 2.07.

B. Green petroleum coke is an electrical insulator whereas elemental carbon (calcined petroleum coke) is an electrical conductor. For example:

   Electrical Resistivity of Green Petroleum coke is 9 x 10^6 ohm-inches.

   Electrical Resistivity of Calcined Petroleum coke is .035 ohm-inches.

C. There are corresponding changes in the X-ray diffraction pattern.

While there are profound changes occurring during the chemical conversion of green petroleum coke to elemental carbon, the mineral matter as indicated by the ash content remains essentially unchanged. The composition of the ash is important as this will affect the type of aluminum metal which can be produced.

The metallic components which are present in the crude oil will be carried over into the coke. Materials such as vanadium and nickel occur in crude oils in varying amounts depending on the area of origin. There is actually very little if any iron or silicon in crude oil. Iron which is found in petroleum coke comes primarily from corrosion of the pipes and vessels used to process the crude oil. Additional iron finds its way into the coke in the form of rust from rail cars and conveying equipment. Silicon can come from the catalyst used in refining also from sand or gravel contamination.

Iron and Silicon in Calcined Petroleum Coke

The iron in calcined petroleum coke will normally range between .01 and .06%. The silicon content will range between .01 and .05. Table II shows the car analysis of iron and silicon in calcined petroleum coke all loaded from the same storage silo. The samples were taken from a conveyor belt with an automatic sampler. In this group of cars, we find some individual cars with iron as low as .019% and silicon as low as .010%. This information is useful to the carbon plant superintendent of a prebaked plant. If he is required to supply anodes which are low in iron or silicon, he can select the cars from a given shipment and segregate the low ash material in a separate area of his storage shed.

Since the iron in calcined coke is magnetic, further removal can be accomplished at the consumers' plant by using magnetic separators. This will be most effective if applied after the grinding operation since iron pick up does take place in equipment such as the ball mill.

Several aluminum plants are now asking for a special grade of carbon with very low silicon. This is a difficult requirement to control at an ordinary calcining plant. However, a substantial improvement can be accomplished by screening the coke and using the coarse fraction for the low silicon application. An example of the degree of improvement which can be achieved by this method is shown in Table III. The silicon bearing material is concentrated in the fines (minus ¼"). The plus ¼" fraction contains only 40% of the total silicon or .008%.

SUMMARY

In summarizing the information just presented, we find that a reasonable amount of care should be exercised at each step of handling petroleum coke. It is recongnized that some of the physical properties (sizing) of a calcined coke can be destroyed if the cutting operation is not carried out properly. Also sources of contamination should be avoided in order to keep the iron and silicon content within required limits. Where a carbon aggregate with low silicon or low iron is required a selection can be made from a given shipment if the material is delivered in rail cars.

References

1. Trammell, W. D., Glaser, D., Oil and Gas Journal p. 65, June 5, 1961.

2. Wright, P. G., Oil and Gas Journal p. 93 - 94, Aug. 11, 1958.

3. Maas, R., Lauterbach, R. E., Petroleum Engineer p. 110 - 124, Feb. 1947.

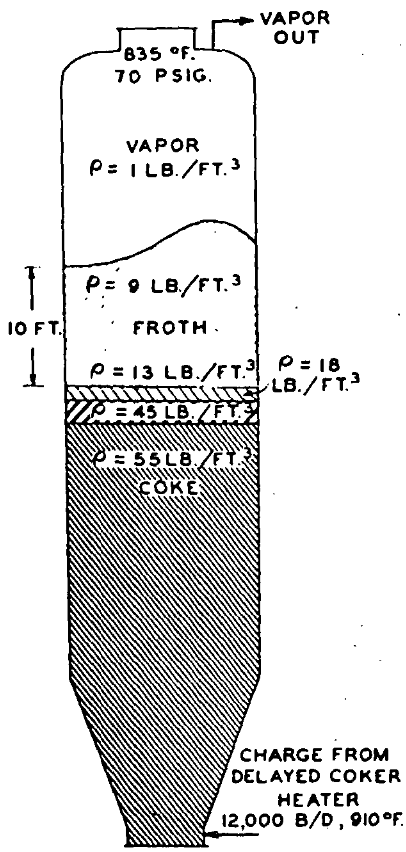
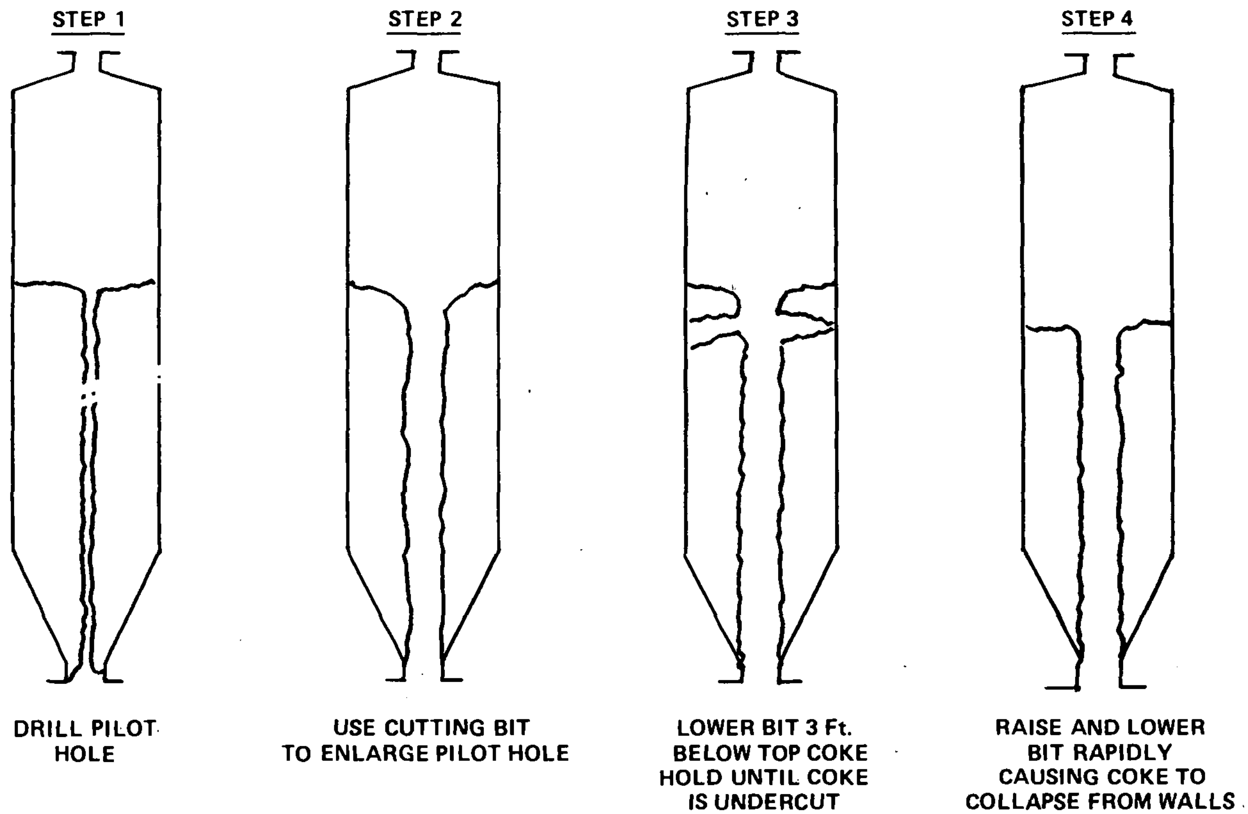

VAPOR OUT
835 °F.
70 PSIG.
VAPOR
ρ = 1 LB./FT.3
ρ = 9 LB./FT.3
10 FT.
FROTH
ρ = 13 LB./FT.3
ρ = 18 LB./FT.3
ρ = 45 LB./FT.3
ρ = 55 LB./FT.3
COKE
CHARGE FROM
DELAYED COKER
HEATER
12,000 B/D, 910°F.

Figure 1.

Figure 2

RECOMMENDED DECOKING PROCEDURE



STEP 5 – REPEAT STEPS 3 AND 4 UNTIL DRUM IS EMPTY

STEP 6 – CLEAN DRUM WALLS

TABLE I

TYPICAL ULTIMATE ANALYSIS OF GREEN PETROLEUM COKE AND CALCINED PETROLEUM COKE

	Green Petroleum Coke (Polymerized Residual)	Calcined Petroleum Coke (Pure Carbon)
CARBON	91.80	98.40
HYDROGEN	3.82	0.14
OXYGEN	1.30	0.02
NITROGEN	0.95	0.22
SULFUR	1.29	1.20
ASH	0.35	0.35
CARBON-HYDROGEN RATIO	24	910

TABLE II

ANALYSIS OF CALCINED COKE SHIPMENTS CARS LOADED FROM PRODUCT SILO

ORDER OF LOADING CAR NO.	ASH %	IRON %	SILICON %
1	.24	.019	.010
2	.21	.021	.012
3	.40	.065	.028
4	.42	.073	.022
5	.34	.043	.025
6	.24	.030	.010
7	.23	.020	.015
8	.33	.035	.025
9	.41	.065	.015
10	.26	.041	.021

TABLE III

EFFECT OF SCREENING ON SILICON CONTENT OF CALCINED PETROLEUM COKE

SIZE	% SILICON
Run of Kiln	.021
Plus ¼ Inch Fraction	.008
Minus ¼ Inch Fraction	.022